

HISTORY OF DEVELOPMENT OF SYNTHETIC FIBRES

Synthetic fibres which have revolutionized the textile industry are the products of science and technology. A number of scientists worked hard in the laboratories to develop these fibres. Leading the list of scientists who have contributed to the development of synthetic fibres is Wallace H. Carothers, who discovered the first synthetic fibre Nylon 66 in the laboratories of DuPont in 1937. Paul H. Slack of IG Farbenindustrie invented Nylon 6 in 1938. Whinfield and Dickson of Calico Printers' Association UK discovered Polyester fibre which was first produced by ICI in 1950. The acrylic fibre was developed by DuPont in 1945 on a pilot plant scale. In 1954 Natta and Ziegler patented a process for producing polypropylene fibre industrial production of which was started by Montecatini S.p.A. in Italy in 1957. The PVC fibre PECE was developed in Germany during second world war. PVAH fibre was produced in 1957 followed by the production of polyurethane elastomeric fibre in 1958.

The first synthetic fibres were rodlike long filaments with metallic lustre. The fibres were dulled with the addition of TiO<sub>2</sub>. These cross sections were astered to improve the glitter or to impart dullness and soft feel. They were crimped and permanently textured. The ionic character of the polymer was modified to impart or eliminate affinity to given class of dyes. Hollow fibres, Bicomponent fibres, mass colored fibres, fibres with microcreations on the surface, elastomeric fibres and fibres with specific elongation at break was produced to achieve the desired textile effects.

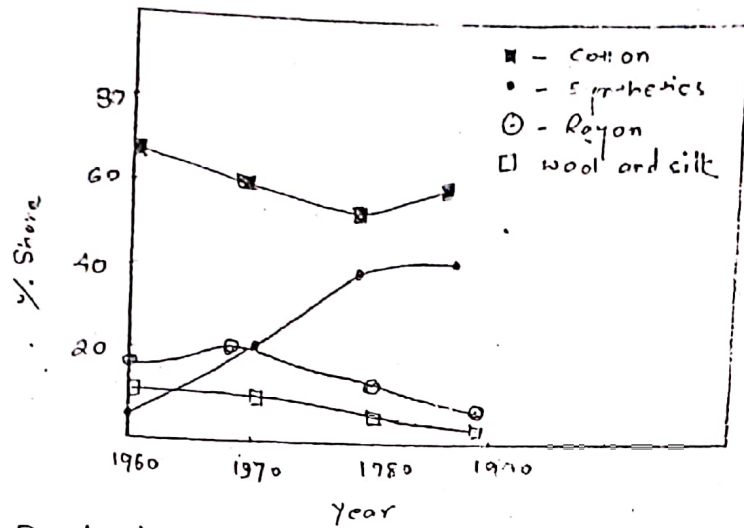
GROWTH OF SYNTHETIC FIBRE IN LAST 35 YEARS

(in 1000 tonnes)

Year	Cotton	Wool and silk	Synthetic fibres	Cellulosic Regenerate	GRAND Total
1950	6650	1170	70	1610	9500
1960	10113	1463	702	2656	14937
1970	11686	1643	4701	3431	21461
1980	13991	1663	10476	3242	29372
1985	17540	1732	12515	2999	34786

1	2	4	5	7	8
1/2	✓	✓	1/2	✓	✓

## World percentage share of various fibres



Production shown by circular diagram

## Unique Properties of synthetic fibres

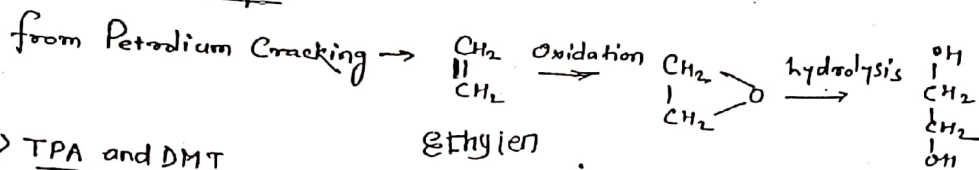
- ① High strength and greater durability
- ② Better crease recovery
- ③ Elegant appearance
- ④ Better dimensional stability
- ⑤ Bacterial resistance
- ⑥ quick drying property
- ⑦ Lesser degradation during washing
- ⑧ Properties of synthetic fibres can be ~~adjusted~~ altered
- ⑨ No demand of fertile land

## Future of Synthetic Fibres

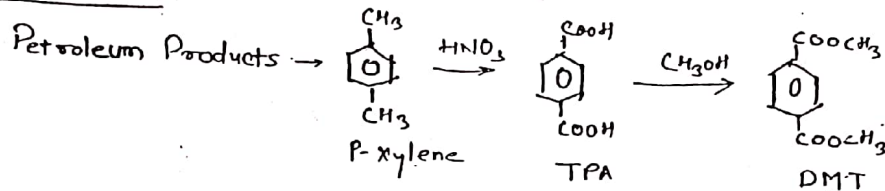
Future of synthetic fibres appears to be quite bright as these fibres are accepted by the consumers and unlike other fibres these production can be easily increased by the turn of this century. Synthetic fibres are likely to account for 60% of

## Production of raw materials (Ethylene Glycol & TPA and DMT)

### 1) Ethylene Glycol



### 2) TPA and DMT



## Properties of raw materials:- (Requirements)

### DMT

MP -  $141^\circ\text{C}$

BP -  $280^\circ\text{C}$

Acid no. - 0.2

Halogen content - Trace

Fe content  $\rightarrow$  0.0005%

$\text{N}_2$  content - 0.00005%

### MEG

BP =  $195 - 198^\circ\text{C}$

$\rho = 1.110 - 1.112 \text{ g/cm}^3$  at  $20^\circ\text{C}$

$n_D^{20} = 1.4330$

$\text{H}_2\text{O}$  content = 0.1%

Halogen = Trace

### TPA

Total Metal = 9 PPM

Ash = 15 PPM

Water = 0.2 PPM

Particle size distribution = 50-600  $\mu\text{m}$

## Production Process :-

To obtain high molecular weight which is essential for fibre production, it is imperative that the two monomers are present during the reaction should be in equilibrium (1:1) proportion. Otherwise low molecular wt. is the result.

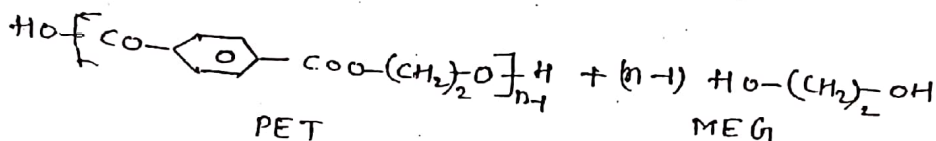
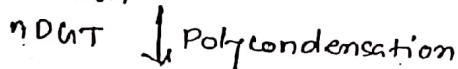
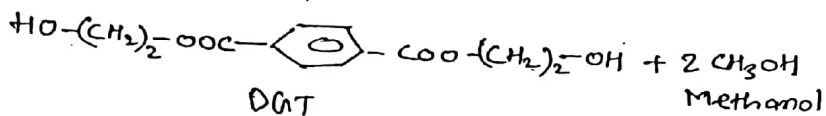
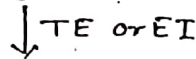
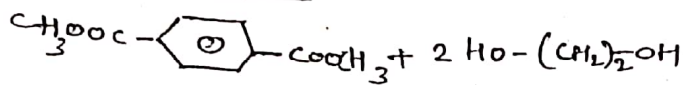
To ensure this stoichiometric ratio of 1:1 a preliminary reaction is conducted between two monomers (DMT and MEG or TPA and MEG) producing new intermediate Di-glycol terephthalate (DGT). In DGT acid glycol ratio is chemically fixed at 1:2. This is the first stage in the production of PET.

The process involves in DMT + MEG reaction, if required to as Ester interchange (EI) or transesterification (TE) on the other hand direct esterification occurs if MEG + TPA are used.

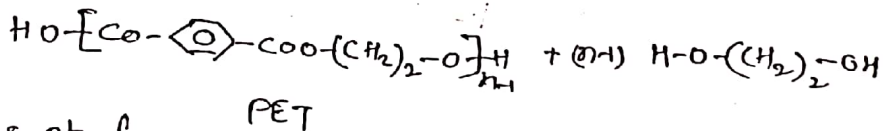
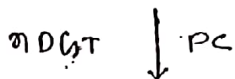
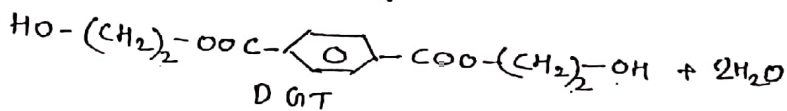
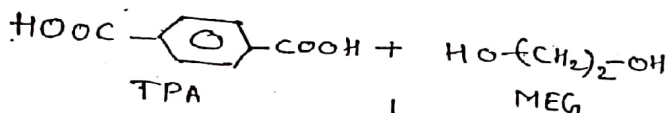
# Production by DMT & TPA routes

## Chemical Reactions involved

### ① TE - DMT Route



### TPA Route:-



## Advantages of formation of intermediate DGT

- 1) Polycondensation is applied to uniform pure monomeric material
- 2) Wider choice of catalysts
- 3) Less side reactions
- 4) High speed of reaction
- 5) Good color polyester
- 6) Better thermal stability of melt
- 7) Better drawability

Overcome some of their limitations so that they will satisfy the demands of the consumer such as comfort, aesthetic properties and ease of dyeability.

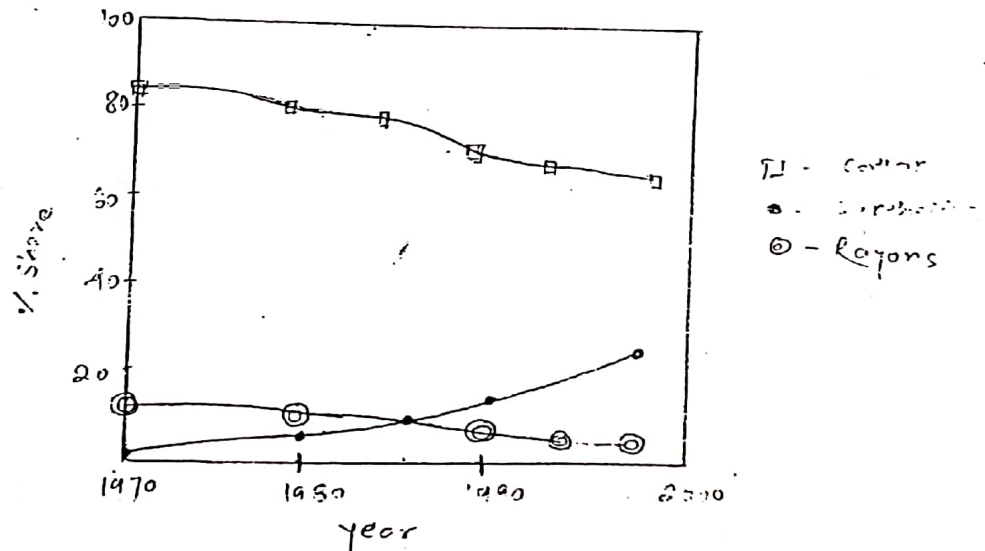
SYNTHETIC FIBRE IN INDIA

in 1000 tonnes

Year	Cotton	Wool	Silk	Regenerated	Synthetics	Total
1960	750	30	1.65	42.50	—	824.15
1970	804	33	2.91	101.02	(1962)	961.56
1980	1191	35	5.00	198.20	59.92	1469.12
1990	1800	43	11	160	490	2504
1995	1870	46	15	190	800	2927
2000*	2040	50	20	230	1125	3465

\* - Projections

India - % share of various fibres



As far as individual synthetic fibres are concerned polyester fibre accounted for 64% of total synthetic fibre production in India. Nylon for 23% and acrylic for 13% in 1985 and Polypropylene for 2%.

# IMPORTANT OPERATIONS IN PRODUCTION OF SYNTHETIC FIBRES POLY-(ETHYLENE TERAPHTHALATE) :- PET

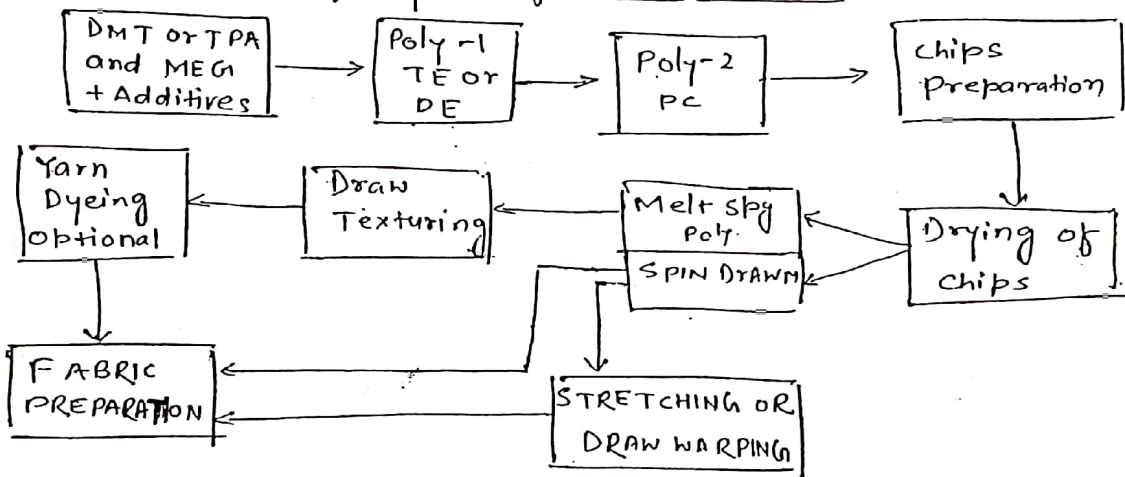
Introduction :- PET is most outstanding member of polyester fibre. PET production has shown the maximum growth rate and it is leading manmade fibre. In 1986 PET constituted 20% of the world fibre demand and 40% world MMF Production.

Definition :- According to ISO PET is defined as polymer containing "synthetic linear macromolecules having in the chain at least 85% (by mass) of an ester of a diol and Terephthalic acid".

The Pioneering work of W.H. Carothers is in the U.S.A. during 1928-1932 on condensation polymers led to the growth of polyester fibres.

## MANUFACTURING

Flow diagram of Polyester filament production



### Two Routes :-

1) DMT Route :- Raw materials are Dimethyl terephthalate and Ethylene glycol (EG)

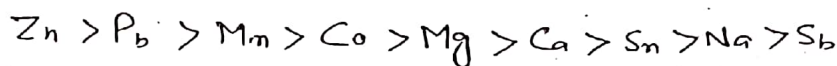
2) TPA Route :- Raw materials are Terephthalic acid and Ethylene glycol.

In early days (1940s) aliphatic dicarboxylic acid and glycol was used to produce the polyester but they had  $M_p < 100^\circ\text{C}$ . Work was continued later by Schelack and Brijojn Whinfield and Diskson continued the work and found aromatic dicarboxylic acid, i.e. TPA was used, for the production of polyester fibres. This product has high  $M_p$  and which did not hydrolyse in boiling water. Both  $\text{HO}-(\text{CH}_2)_2\text{OH}$  and  $\text{HO}-(\text{CH}_2)_4\text{OH}$  is used. But now only  $\text{HO}-(\text{CH}_2)_2\text{OH}$  fibres produced by using  $\text{HO}-(\text{CH}_2)_4\text{OH}$  is called 'Kadai' fibre.

## Process via DMT Route

In this route first step is  $\text{TE}$  followed by  $\text{PC}$ .

Catalysts :-  $\text{TE}$  involving  $\text{MEG}$  and  $\text{DMT}$  is slow process and requires a catalyst to enhance the process. The catalysts are usually (i) metal oxide or a metallic salt. Usually metallic metal oxide or metal salt of weak or volatile acid is used. The catalytic activity of most commonly used metal acetates are shown below

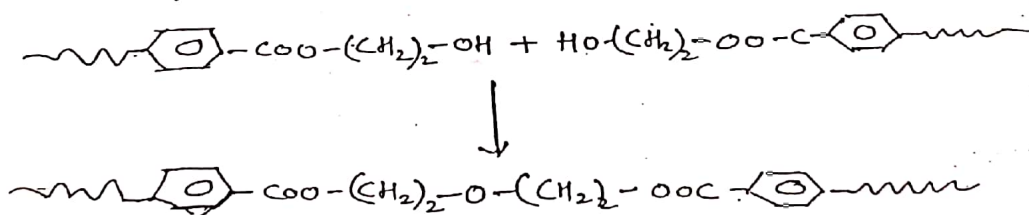


First one is highly active and last one is least active. Both the extremes are not applicable so to have a balance some times combination of two catalysts are used. The catalyst amount is 0.02 - 2% and catalysts should be deactivated during  $\text{PC}$  stage otherwise it activates the degradation. It is done by adding  $\text{TPP}$ ;  $\text{TNPP}$  during  $\text{PC}$  stage which converts catalyst to phosphorous derivative which is not active.

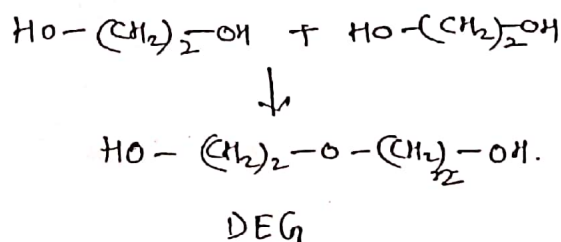
$\text{Sb}_2\text{O}_3$  is the unique catalyst which is used in the  $\text{PC}$  stage which does not degrade  $\text{PET}$ , but it may get reduced to metallic  $\text{Sb}$  by action of phosphorous stabilizers imparting a grey green colour to  $\text{PET}$ . So if while  $\text{PET}$  is required  $\text{GeO}_2$  is used as a catalyst in  $\text{PC}$  stage.

Side Reactions in EI-Step and DE-step :-

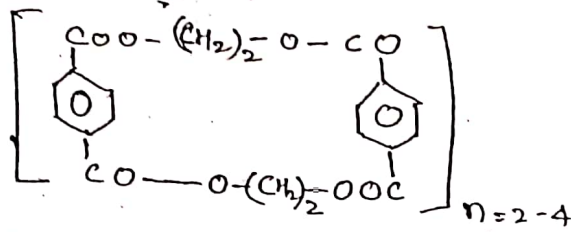
(1) Ether group formation :-



(2) Reaction b/w two  $\text{EG}$  to form  $\text{DEG}$



### ③ Some oligomer formation



### Factors contributing to formation of side products

- ① Low rate of esterification of TPA
- ② Low pH
- ③ Variation of PC temperature

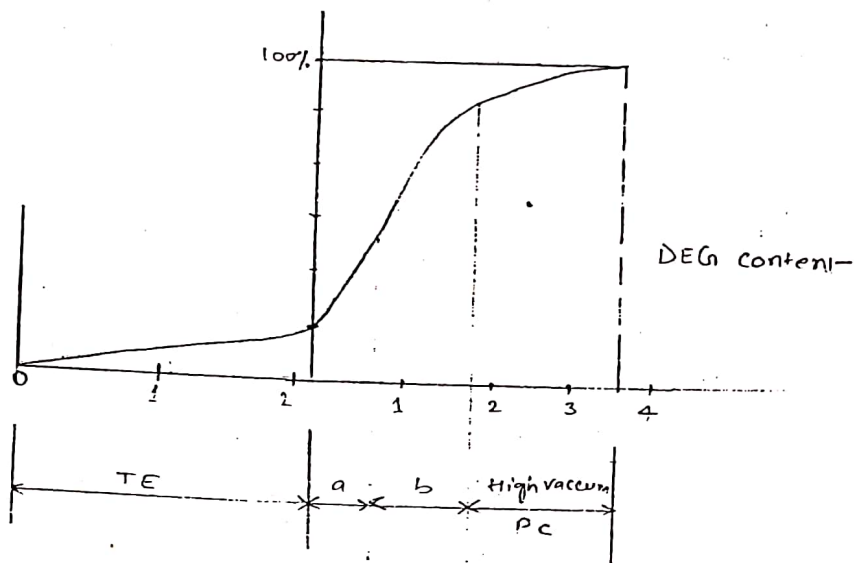
### Effects :-

- 1) Melting Point is lowered
- 2) ~~Mol wt~~ Molecular Wt is lowered
- 3) formation of amorphous pockets in Polymer.
- 4) Dyeing rate increases
- 5) Tensile strength of fibre is lowered
- 6) Resistance to light and thermoxidation decreases
- 7) Wash and wear properties are affected.
- 8) Yellow colouration due to formation of COOH end groups.

### Minimising :-

- 1) Use of thermal stabilisers
- 2) low pressure and short diffusion path in PC stage.
- 3) Addition of 0.5 - 2% diphenyl ester at an intermediate stage of PC.





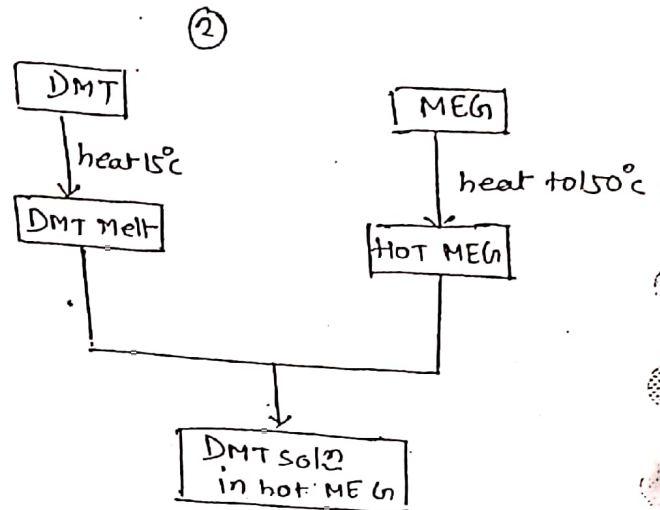
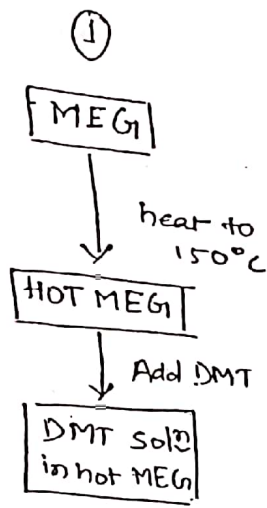
Rate of DEG formation at different stages of PET Synthesis (a) Pre-heating (b) Low vacuum

Most of DEG is formed during preheating and low vacuum stage of PC. Only about 20% is formed during TE and 5-10% formed during final stage of PC. DEG is mostly likely to be immediately removed from the reaction mixture by distillation, ~~therefore~~ since of its rather high Bp (245°C) it will enter the PET chain in the form of 3-oxipentamethylene units. This PET is essentially a co-polymer having DEG units occurring in between PET.

DEG formation can be reduced by the addition of tetraethyl ammonium terephthalate, lithium acetate, sodium carbonate, NaOH etc during esterification reaction between TPA and MEG. DEG content can also be controlled by taking minimum possible amount of MEG for Esterification reaction. Proper stirring and temperature programming is also helpful in controlling the formation of DEG.

Process :- Dissolution of DMT in MEG

The EI Process is proceeded by dissolution of solid DMT in MEG. This can be achieved by two ways.



Advantages of Process two over one :-

- ① Solid is produced more rapidly
- ② Pre melting of DMT provides better stability to melt.
- ③ Side reactions are less
- ④ Dwell time in kettle is less.

Ester interchange reaction:-

Steps

- ① Add DMT + EG solid with Mix  $TiO_2$  suspension of particle size  $0.5 - 1.5 \mu m$ .

grades

- ① bright
- ② Dull
- ③ semidull

$TiO_2$  types

- Anatase (used in fibre industries)
- Rutile

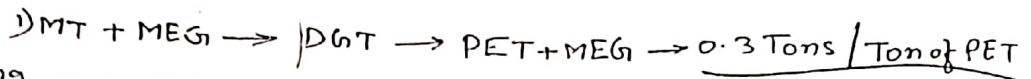
Amount - 0.5% by wt. of polymer is used.

$TiO_2$  absorbs light falling on fibre there by giving ~~dull~~ dullness to fibre. As the amount of  $TiO_2$  increases the light absorbed will increase and light stability decreases. If amount of  $TiO_2$  is increased it may enhance the degradation and may change the colour.  $TiO_2$  should be in the form of slurry while adding.

- ② Catalysis - Added in the form of dispersion. 0.02-2%. If catalyst amount is increased the rate of degradation increases.

(3) Ratio of DMT:EG

If 1:2 is used

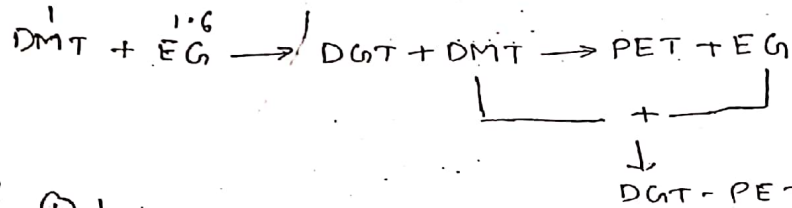


Taking out MEG consumes considerable amount of energy, time, money etc.

So not to use 1:2

Use 1:1.6

in this case



So

- ① Less recovery
- ② Less handling
- ③ Less consumption
- ④ Less cost
- ⑤ Energy saving
- ⑥ Less degradation due to less time taken for EI.

④ N<sub>2</sub> atmosphere :- To avoid thermo-oxidation, the N<sub>2</sub> atmosphere should be created in the beginning i.e. initial condition of feeding.

⑤ Agitator speed :- 40-50 rpm should be spark free.

⑥ Reaction temperature :- (a) 150°C without reflux  
(b) 195°C with reflux

Reflux

Without - 150°C

With > 195°C BP of EG is 197°C

150°C advantages

- ① Temp. is less, larger time for reaction and more control over process.
- ② Less side reaction

Disadvantages :- ① As CH<sub>3</sub>OH evaporates it takes DMT along with it thereby clogging the pipe.

② Pollution is less

But at  $195^{\circ}\text{C}$  the MEG starts boiling. Along with  $\text{CH}_3\text{OH}$ , DMT and EG also evaporates. In pipe EG gets condensed and wash away the DMT which is clogged on the inner surface of pipe.

(2) Reactions faster so less time and high production.

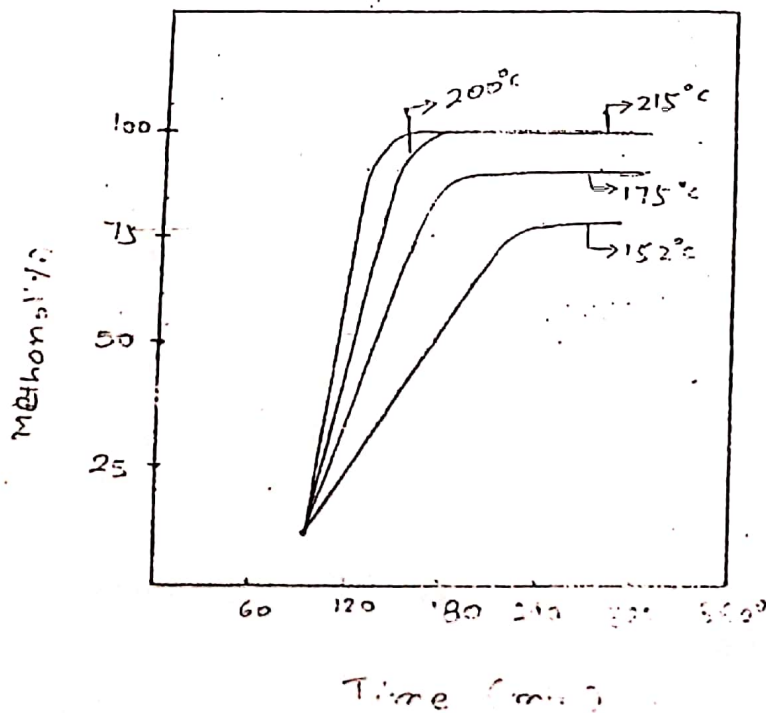
(7) Time :- 3-6 hrs

(8) At the end the temperature is maintained between  $200$  to  $205^{\circ}\text{C}$  and then the temperature is raised to  $240^{\circ}\text{C}$  before passing the transesterified product to PC vessel. The ~~important~~ temperature is raised in 3-4 steps ( $10^{\circ}\text{C}/\text{step}$ ). The stepwise increase in temperature has following advantages

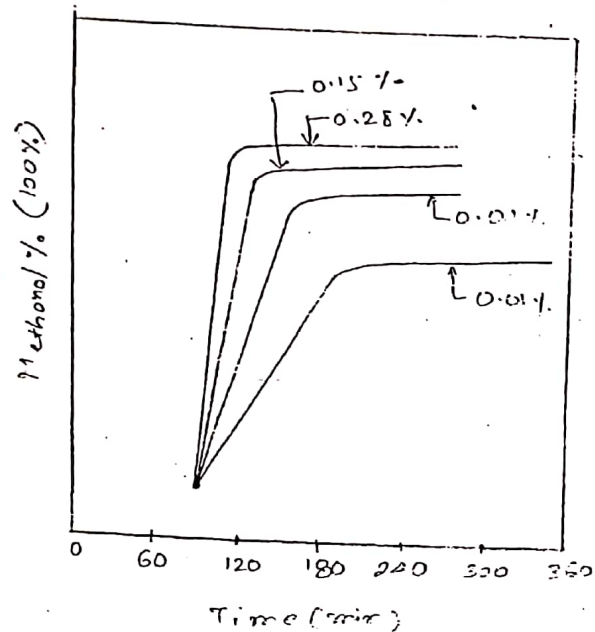
!- (1) Reaction starts slowly.

(2) TE continues, Residual  $\text{CH}_3\text{OH}$  can still be removed. EG starts plotting and reacting with DMT.

Effect of Temp<sub>1</sub> on the Course of EI (Zincacetate + PbO-0.2%)



Effect of Catalyst Concentration on the rate of TE  
(Zn acetate + PBO - 2:1)



Direct esterification :- TPA Route

Advantages of TPA OVER DMT

- ① Cost of TPA < DMT
- ② By-product methanol is not formed
  - (a) recovery of  $\text{CH}_3\text{OH}$  is difficult
  - (b) Poisonous
  - (c) inflammable (BP-56°C)
  - (d) In industry this recovered methanol is treated as second grad one.
- ③ No need of catalyst
  - (1) No catalyst production
  - (2) contamination due to catalyst is not there.
- ④ Superior product quality
- ⑤ High mol. wt. can be obtained
- ⑥ TPA gives 15% higher yield
- ⑦ Less capital investment for plant construction (20%)
- ⑧ Less EG required
- ⑨ Less time required
- ⑩ High bulk density of TP requires less storage space

### DISADVANTAGES :-

- (1) Difficult to handle
- (2) Can not be easily pumped or transferred in molten form.
- (3) Reaction proceeds in hetero phase due to poor solubility of TPA in EG leading to non-uniformity in the product. Efficient stirring is required.
- (4) High proportion of by-product is formed (DE = 2-8% , TE = only 1.8%)
- (5) Water liberated may act as plasticizer and reduced the length strength of PET.
- (6) High pressure and vacuum system necessary.

Catalyst :- TPA itself accelerates the reaction. So the degradation reaction is less. But some degradation reaction parallel to TE occurs in DE also.

Process :- Solubility of TPA is low in EG. It requires a temperature of 240-260°C at a pressure of 4 atm to prepare the mixture in the proportion of 1:1 to 1:1.3. The process proceeds smoothly and byproduct water is ~~dissolved~~ distilled off from the system. So, No reflux system is necessary. When the process is complete the thermal stabilisers are added to the low [η] melt before transferring the melt to the PC stage. Hence the ether formation tendency is moved in this case.

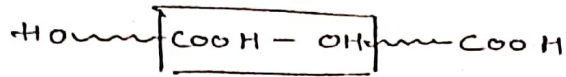
### POLYCONDENSATION [Mol. wt. = 20,000 for fibre grade]

PC stage is same for both DMT and TPA route. If necessary a second dose of catalyst is added here. "The attainment of final molecular wt. of the polymer is not chemically controlled but controlled by diffusion". Hence the ~~polyester~~ progressive reduction in ~~presence~~ pressure up to 0.2 mm of Hg (25) is made to obtain a high mol. wt. polymer.

Temp = 280-290°C. EG formed has to be removed during the reaction. PC should be completed quickly.

- ✓ Points :-
- (1) Temp = 280° - 290°C (with stabilizer)
  - (2) Apply vacuum to remove MEG
  - (3) Allow diffusion to take place easily so that heat transfer takes place quickly.
  - (4) Decrease the pressure progressively to 0.2 mm Hg (25 Pa)

## Ether Formation



At 99% Conversion DP = 100

If conversion of monomer is increased DP ↑.

Limit :- Hold the product at higher temperature. The reaction takes place given :-



If the time of PC is increased the mol. wt. increases.

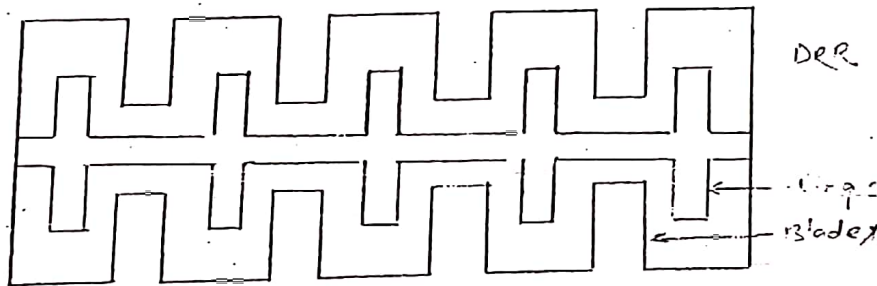
Limit :- If time is increased tenacity decreases. At more time H<sub>2</sub>O content gets increased and viscosity increases, diffusion of H<sub>2</sub>O molecules becomes difficult and H<sub>2</sub>O starts hydrolysing PET.

So the time can be reduced by ① increasing temperature

② Decreasing pressure

③ Make diffusion path easy.

Reactor :- Disc ring reactor (DRR). This is the finest reactor for final PC. The melt from the prepolymeriser is pumped to



DRR by means of gear pumps. In the reactor there are series of discs fitted on a shaft which revolves and acts as agitator. There are three temperature zones in the reactor inlet, middle and outlet. Required vacuum can be produced. Assuming esterification is complete the temperature attained, vacuum, agitation concentration and type of catalyst determines the course of PC.

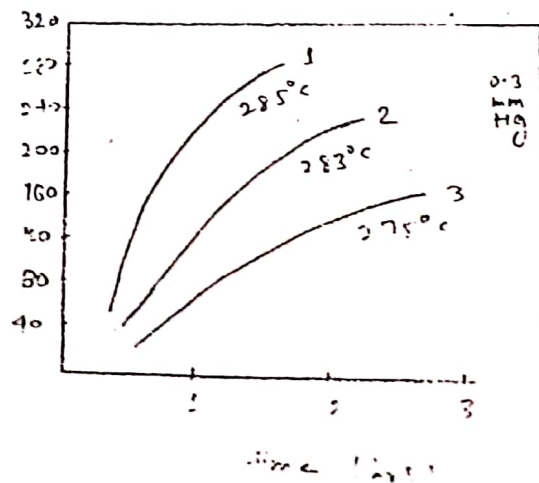
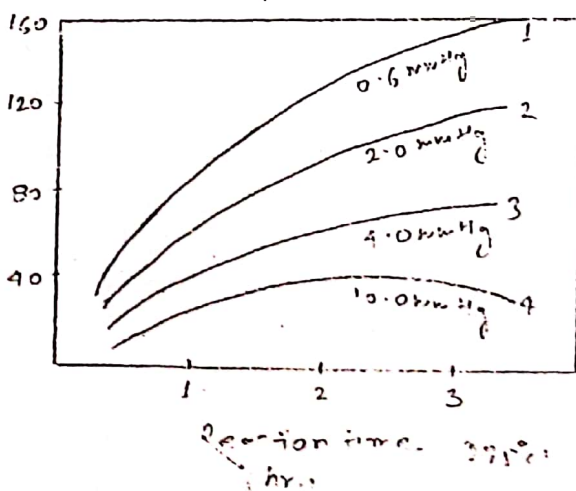
- Advantages :-
- (1) Well mixing of material
  - (2) Well dispersing technique
  - (3) No vortex formation
  - (4) Each disc is separately driven and if one motor is damaged the production can be continued.
  - (5) Control is superior.

Removals

<u>DMT</u>	<u>TPA</u>
Methanol	H <sub>2</sub> O
MEG	MEG
H <sub>2</sub> O	H <sub>2</sub> O

At high vacuum these vapours will come out of the duct provided and they get condensed. MEG should be purified before using further. The oxidation should be avoided in order to avoid the formation of CH<sub>3</sub>CHO.

Polymer is discharged from DRR by means of discharge screw or a gear pipe and then they are extruded in the form of ribbon and then cut into chips and cooled with H<sub>2</sub>O vapours (avoid contamination) and then dried in N<sub>2</sub> atmosphere or vacuum at 120-110°C in dryer rotating at 1-5 rpm. Then they are sent for melt spinning process.





## Continuous Process (Luckert and Stibel 1986)

### Advantages

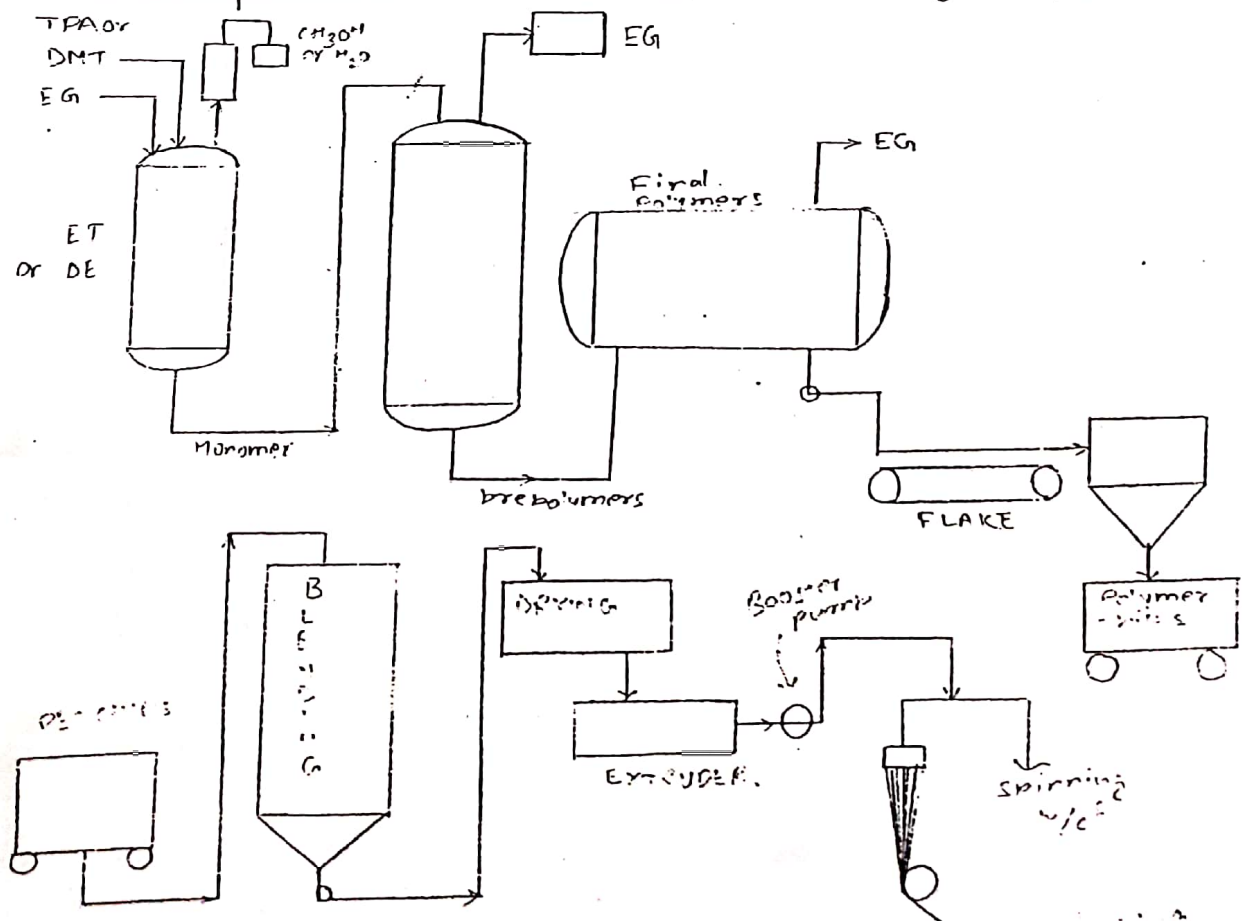
- ① Steady state and easily asseable to automation.
- ② Product of good quality is produced
- ③ Low investment and installment costs.
- ④ Low Producing cost

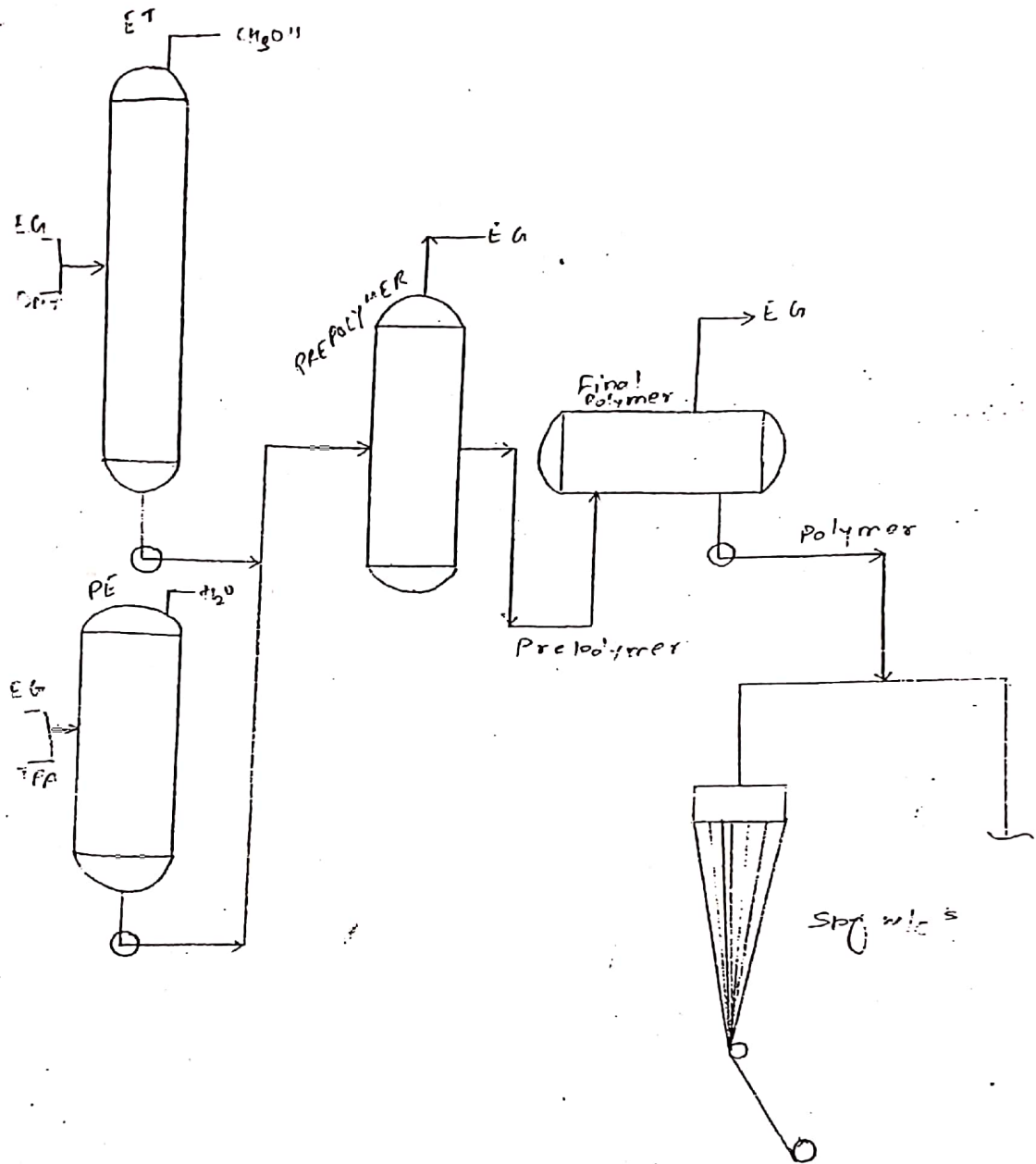
### Disadvantage

- ① In the event of power failure, large amount waste is generated.
- ② Once the process is stopped stabilization of process for restarting requires skill.
- ③ Defect in any one unit leads to production of sub standard product.
- ④ Additional investment cost is required to make the process flexible for preparing speciality fibres.

### FLOW DIAGRAM of Batch & Continuous Process

#### Batch Polymerisation and screwmeter spinning Process





Recent developments between 1985-1994 in PET Production

- (1) Continuous TE/PE and PC with direct spg sections
- (2) Decrease in production of units
- (3) Drying of units is not required as melt is directly taken for spg.

## POLYAMIDES

Introduction :- The two polyamide fibres which have become important commodity fibres are Nylon 66 and Nylon 6 (N66 and N6). Both are based on aliphatic chain. A new class of aromatic polyamides or aramid fibres are also come up, mainly as industrial fibres. These are dealt separately. The pioneering work of Wallace Carothers of the Du-Pont Company in the U.S.A. led to discovery of N66 around 1937. Paul Schlack in W. Germany discovered N6, which is produced through another route, a bit ~~later~~ later in 1939. Both these fibres have had a far reaching impact on the international fibre front.

In India, Nylon 66 fibre is not yet manufactured though it is likely that it will be produced soon. As far as Nylon-6 is concerned there were about 20 production units in India in 1989-1990.

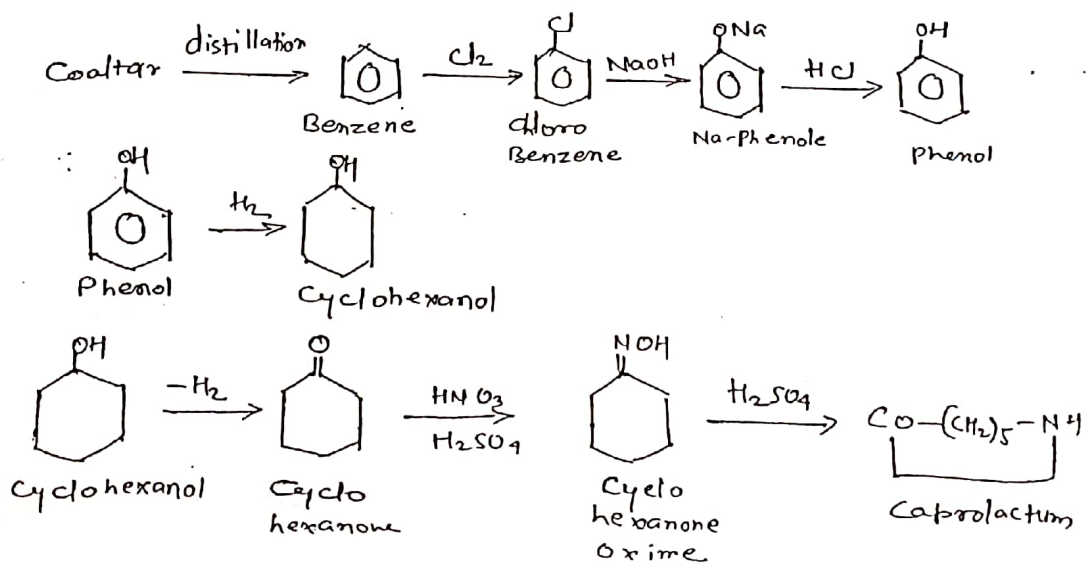
Here in this chapter first the production of nylon-6 polymer is dealt followed by N66.

### Nylon-6

Definition :- Nylon-6 is a member of group of polyamides. The structural units of polyamide is  $-NH-CO-$  groups.

Raw material :-  $\epsilon$ -Caprolactum  $H-N(CH_2)_5-CO (Cl)$

### Synthesis of Caprolactum



Specifications: The crude caprolactum must be carefully purified to have the following specifications.

Mp =  $68.4^{\circ}\text{C}$

Moisture = 0.2%

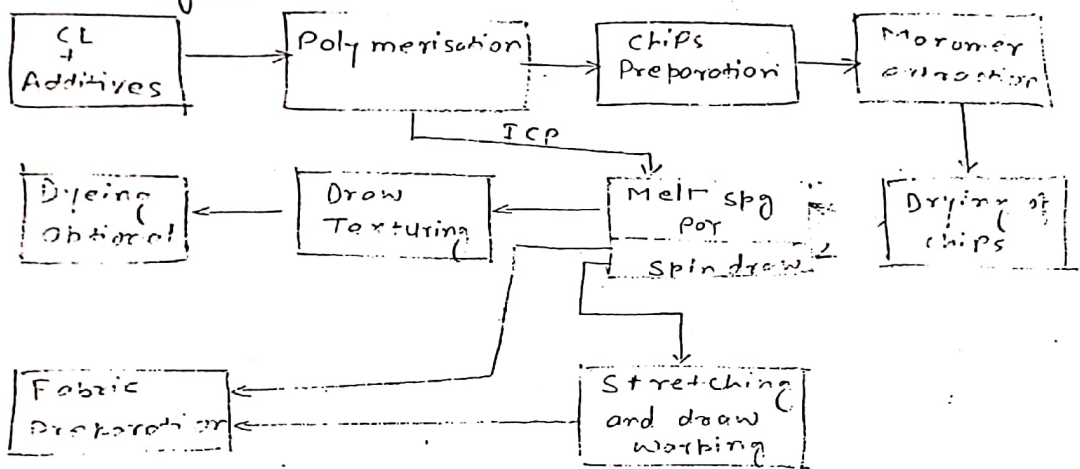
Melt  $[\eta] = 9$  cP. at  $78^{\circ}\text{C}$

Heat of poly $^{\text{m}} = 20$  kcal/mole

Water insoluble compounds absent

Water solution crystal clean

Flow diagram



Types of Catalyst: - CL does not polymerize in a completely dry condition. It requires a catalyst with which converts small amount of CL to Aminocaproic acid (ACA). This is followed by polymerisation. The catalyst can be acid, a base or simply water.

Catalyst systems for CL Polymerisation

Parameters	Acid	Base	H <sub>2</sub> O
Type	Strong like HCl or their salt	Carbonates, nitrides, alcoholate, hydroxides of alkali etc.	—
Rate	fast	very fast	slow
Special condition	Anhydrous	Anhydrous	—
Yield	Low	High	High
Use	Not used commercially	Shows promise	Commercially used

Note:- Base catalyst system gives a good polymer and production rate is very high. However, the control of the reaction is very difficult and high grade of sophistication is required in using technology. In general  $H_2O$  catalysed system is practised in industry.

Parameters of water catalysed system:-

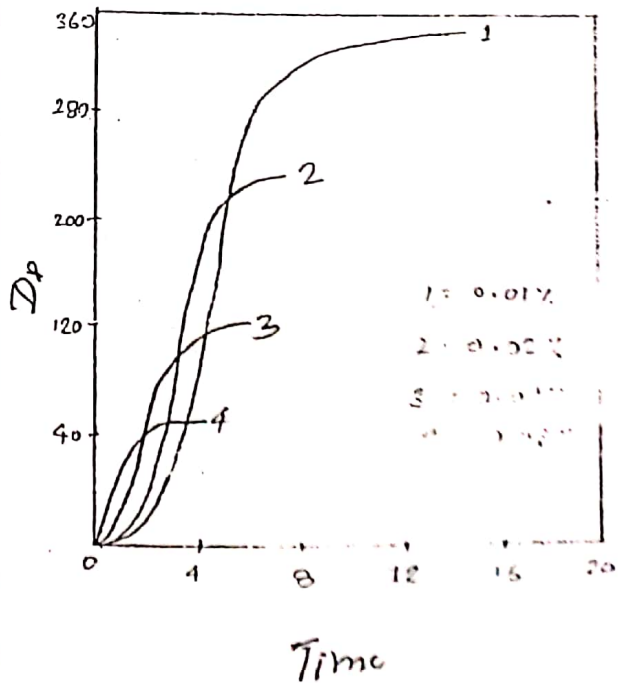
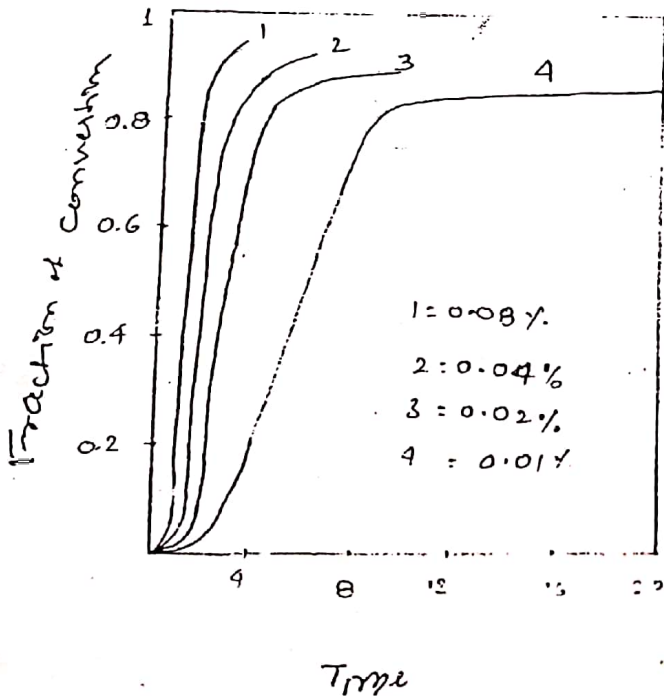
Increase in parameters	Mol. wt.	Time of Polymerisation	End Group
$H_2O$ Concentration	decrease	decrease	increase
Temperature	decrease	decrease	increase
Stabilizer Content	decrease	—	—
Time of Polymerisation	increase	—	decrease

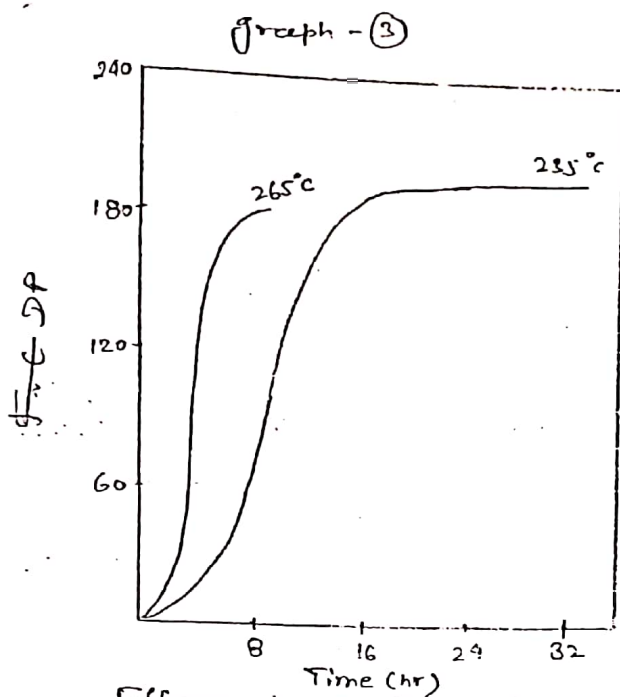
Graphs :-

Effect of initial  $H_2O$  concentration on rate and extent of polymerisation

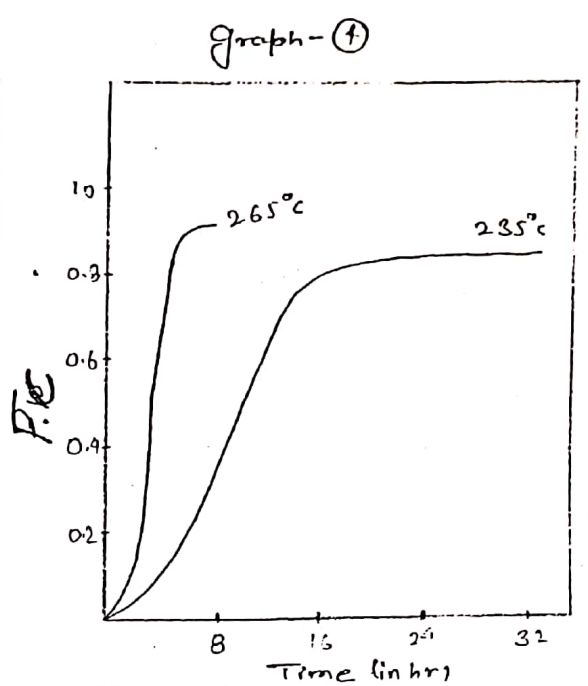
①

Effect of initial  $H_2O$  concentration on D.P.





Effect of T on DP and extent of Polymerisation



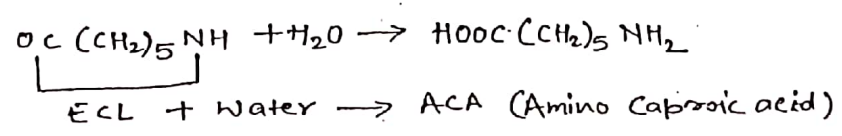
Effect of T on rate and extent of polymerisation

In industrial practice the polymerisation is controlled by :-

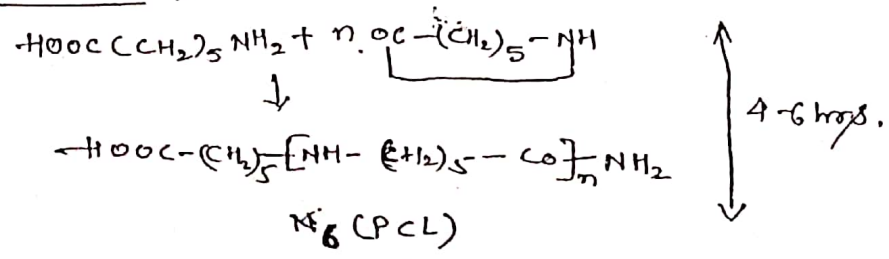
- (1) Temperature in the range of 225°C-280°C and the amount of H<sub>2</sub>O present in the dissolved phase (5-10%)
- (2) So the mol. wt. can be controlled by (a) Temperature (b) amount of H<sub>2</sub>O (c) Time (d) Stabilizer content

Stabilizer :- Up to 1% is required, stabilizer may be acid type (Eg. - CH<sub>3</sub>COOH, Benzoic acid) or basic type (e.g. Benzyl amine). An acid stabilizer leaves the carboxyl and group in the polymer free thus making it reactive to direct dyes. On the other hand use of basic stabilizer yields an acid dyeable nylon.

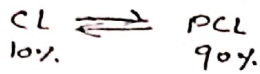
Mechanism :- CL polymerisation is proceeded by a hydrolysis step



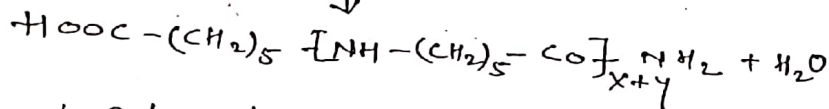
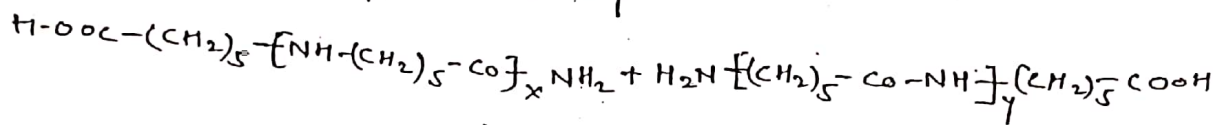
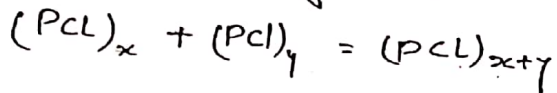
Step addition :-



The process develops on equilibrium after some time of polymerisation, Industrial practice, under optimum conditions, the reaction forms an equilibrium with 90% in favour of PCL.



But at 90% conversion MW is less so the mol. wt. should be further increased by continuing the reaction and mechanism is called "Step Growth Reaction".



Process of Polycondensation :-

① Batch Process :- Not used at present. Used only in research purposes and production of speciality grade fibres.

Disadvantages :-

- 1) less production
- 2) Severe thermal history
- 3) Variation from batch to batch
- 4) Each time batch should be heated to 280°C.

Continuous Process :- V.K. tube process

VK = German word "Verinfacht Kontinuerlich" meaning (continuous)

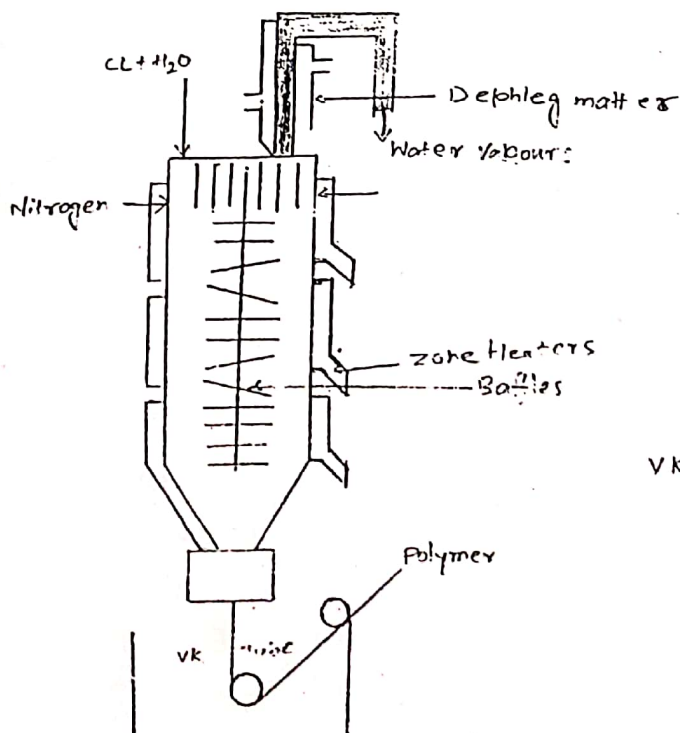
Feed contents :-

- ① Molten CL (MP - 69.8°C)
- (2) H<sub>2</sub>O
- (3) Acid or base stabilizer
- (4) Pigment
- (5) Delustering agent
- (6) Antistatic agent
- (7) Light stabilizers
- (8) Heat stabilizers.

## Advantages of melting CL before feeding:-

- (1) Transfer of solid to high temperature ~~reactor~~ vessel is difficult.
- (2) Metering is easy.
- (3) ~~Align~~ Agglomeration due to instantaneous friction is avoided.
- (4) Controlling  $O_2$  atmosphere is easy.
- (5) No dust problem.

VK tube - It is 8-10 m high having dia depending upon the capacity. The tube is made by assembling several independent sections, each section has its own heating system, (Dowtherm vapour or electricity) and control. Inclined baffles are placed in the tube which force the reaction to take a downward zig-zag course. The angle of inclination and design of these baffles are crucial in determining the course of reaction. Bubble caps are occasionally provided in the baffle plates so as to facilitate escape of volatiles. The topmost zone serves as feed zone and acts as reflux condenser several inlet and outlet pipes are present for feed and out going vapours. At the bottom of the tube a very powerful extruder is placed which continuously pumps out molten  $N_6$  from the VK tube and delivers it in a str. and form to cutter after cooling it to a temperature int above  $T_g$  ( $\approx 60^\circ C$ )



VK = Verinfa-  
Kotenerilich



As the feed enters the top most zone, the molten mixture appears to boil due to water bubbles escaping the liquid phase. The change of course of polymerisation is decided by the temperature at this zone. The material ~~is~~ moved downwards and step addition process is complete within 6hrs. The remaining time (up to 20 hrs) is spent to increase DP. At the end of polymerisation, the highly viscous melt is pumped out by the extruder and cut into chips. The chips are then washed and dried as follows.

Washing :- Nylon 6 polymer chips contains 90% PCL and 8-9% CL and oligomers upto 3-4%. The chips are subjected to counter current washing at 95°C so as to remove CL. This is necessary so as to prevent post polymerisation during melt spinning. The following process variables are important.

- ① Water/polymer ratio.
- ② H<sub>2</sub>O Temperature
- ③ Specific surface of chips
- ④ Time of each washing
- ⑤ Efficiency of the process

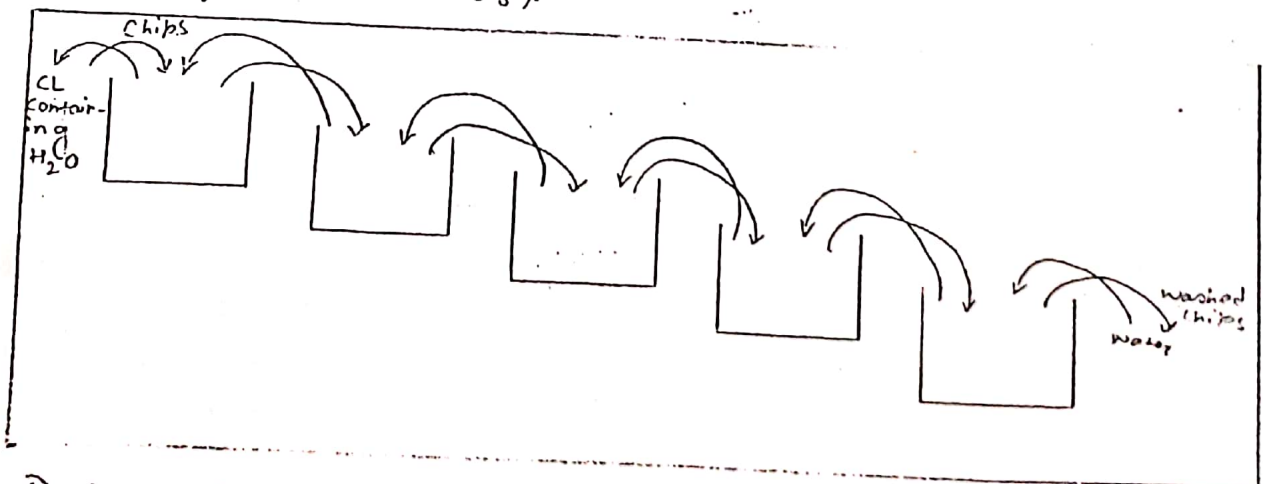
The residual monomer content in the polymer decrease as follows.

After 1<sup>st</sup> wash = 5%.

After 2<sup>nd</sup> wash = 2-5%.

After 3<sup>rd</sup> wash = 1-1.5%.

After last wash = 0.5%.



Drying :- The wet nylon 6 chips are then sent to rotary drum drier operation at 100-120°C either under vacuum (10 torr) or under nitrogen rotating at 1-5 rpm. The drying takes place for 20-50 hr. Yielding chips having residual moisture content 0.02-0.04%. The chips size (3mm x 3mm) are stored under N<sub>2</sub>.

## ICP (Integrated Continuous Process)

### Disadvantages of V.K. tube process

- ① More no. of process required
- ② More energy consumption
- ③ ~~Between~~ Between ~~hand~~ Variation is more
- ④ More handling etc.

The VK tube method was developed in 1950<sup>s</sup>. In 1970<sup>s</sup> a modification of this process slowly built up. The modification was aimed at removing the monomer and the oligomers from the melt by application of vacuum so that melt can be ~~directly~~ directly used for melt spinning. This eliminates the subsequent washing, drying, remelting of the chips during melt-spinning ~~optionally~~ optionally chips can also be produced.

In this process, the melt from the VK tube in incomplete state of polymerisation is spread over a large surface in a thin film evaporator operating under vacuum. This helps in removing the residual monomer quickly and heat transfer is also better. However mol. wt. somewhat increased due to disturbance of the equilibrium. The melt is then led either through an extruder or a cutter to yield chips are directly to melt-spinning.

Efficiency of ICP depends on

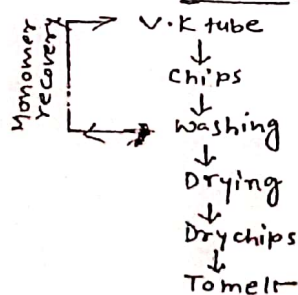
- ① Amount of vacuum
- ② Residence time
- ③ Design of equipment
- ④ Design of Process.

Advantages :- ① Polymer melt can be directly converted to chips or melt SPG

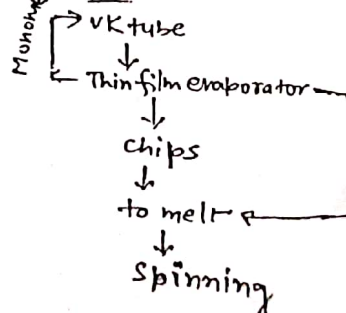
- ② No extraction and drying step
- ③ Monomer recovered can directly recycled to feed.

Disadvantages :- 1) less effective in removing water soluble constituent  
 2) Amount of oligomer retained is more.  
 3) Amount of the soluble material retained in Conventio process 1.7. and in ICP 2-8-3-8 f

Steps :- V.K. tube



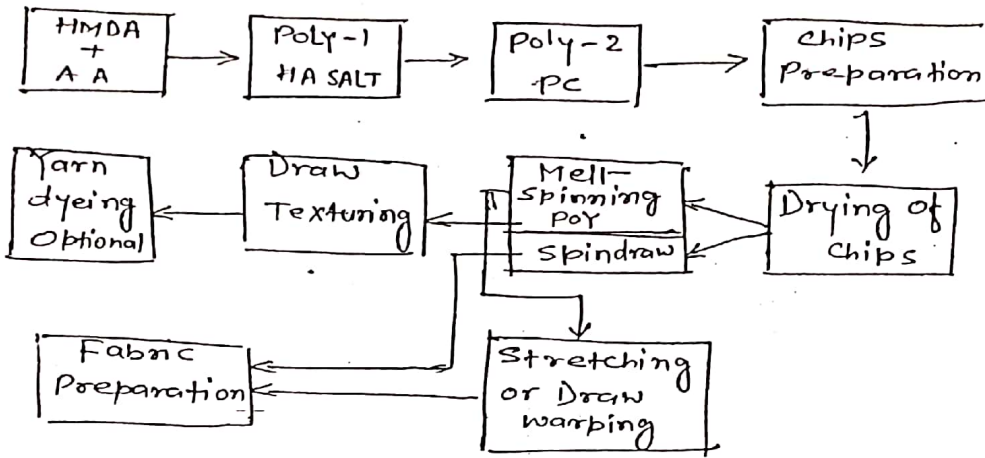
I.C.P



Suitability :- ICP is suitable for producing carpet yarns and continuous filament or staples.

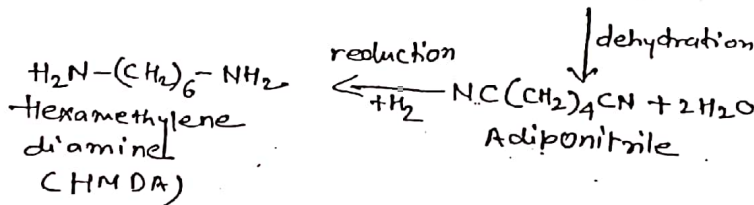
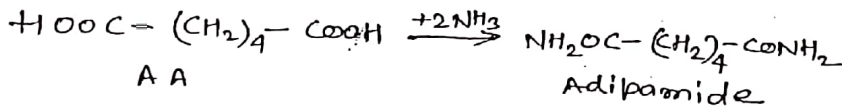
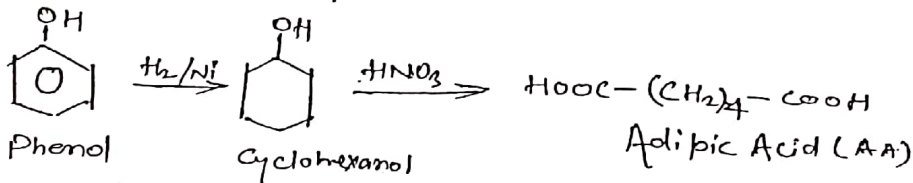
## Nylon 66

### Flow diagram for Nylon filament Production



### Production of Rawmaterials

- (1) Hexamethylene diamine      (2) Adipic Acid



### Requirements :-

HMDA  
 State → solid  
 Colour → colourless  
 Mol. wt. → 116  
 MP → 40°C  
 BP → 204-205°C

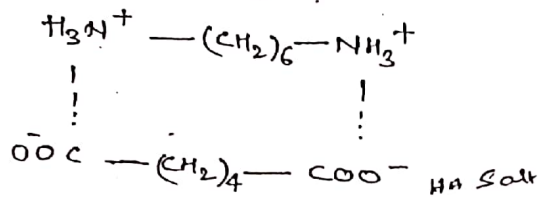
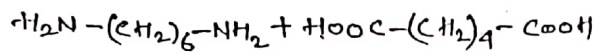
AA  
 State → solid  
 Colour → white  
 Mol. wt. → 146  
 MP → 200°C (≅)

## Production of N66

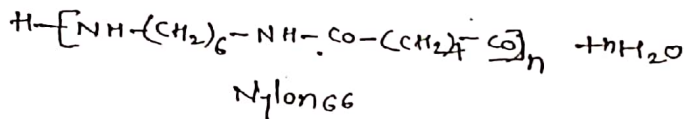
Since the two raw-materials (monomers) in order to obtain high mol. wt. and good quality stoichiometric ratio between amine acid and acid should be 1:1. So as an intermediate reaction is conducted to get a compound called HA salt or Nylon 66 salt in which the stoichiometric ratio between acid and amine is 2:1.

### Reaction :-

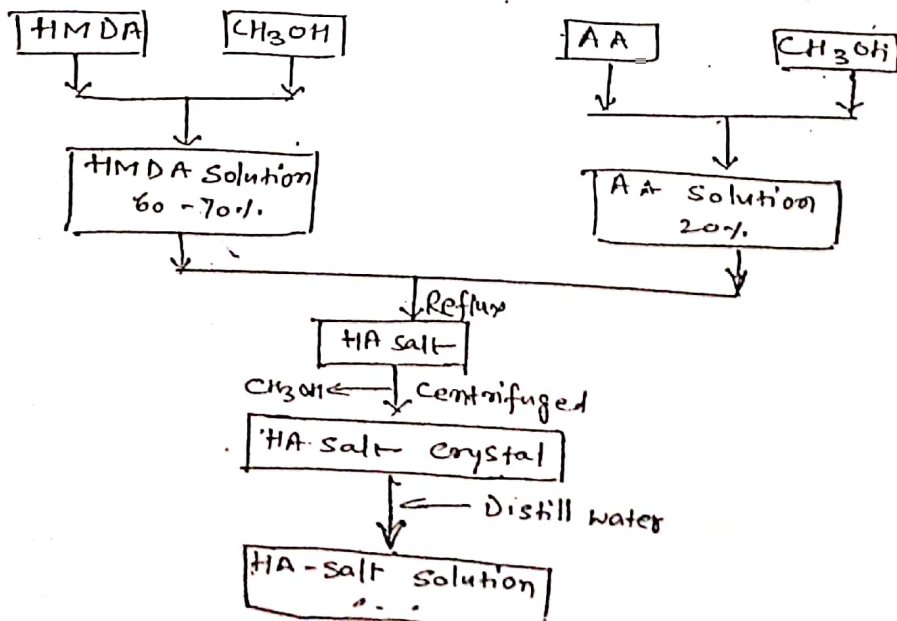
#### Stage One :-



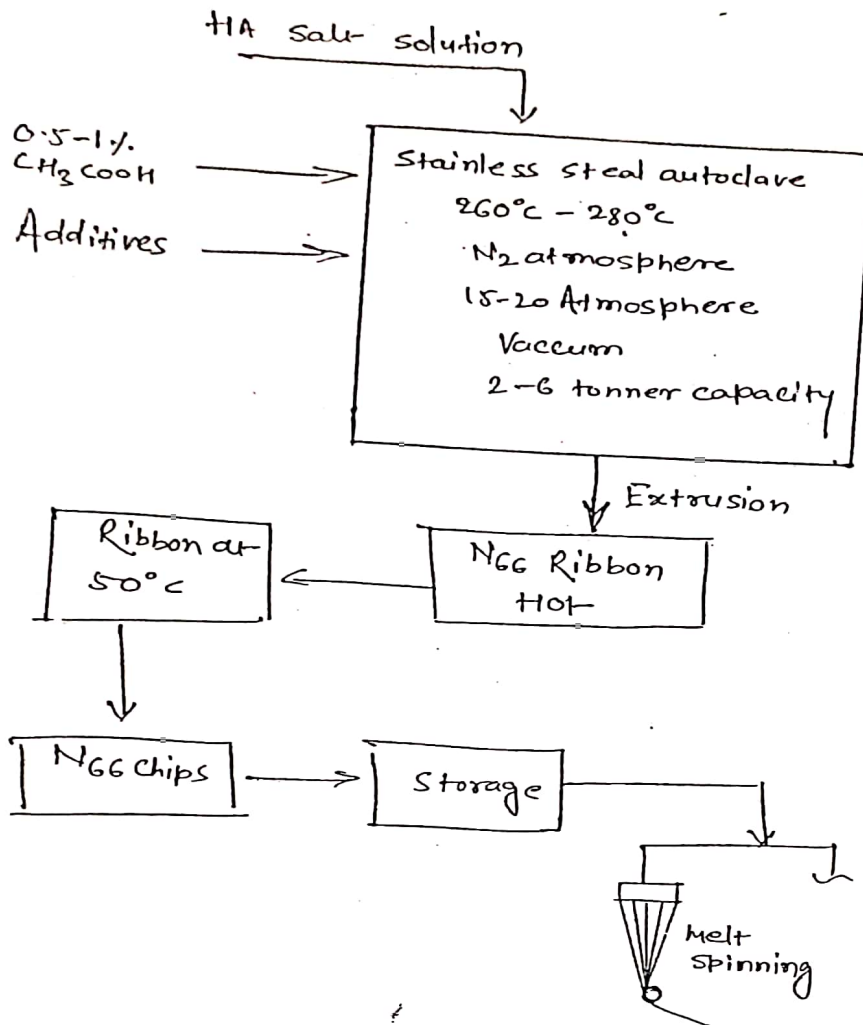
#### Stage Two (Pc)



Stage 1 :- N<sub>66</sub> salt (Neutralization reaction) since there is large difference between mp's of raw materials they can not be melted together after mixing. So they are converted into solution before mixing using methanol.



## II stage Pc

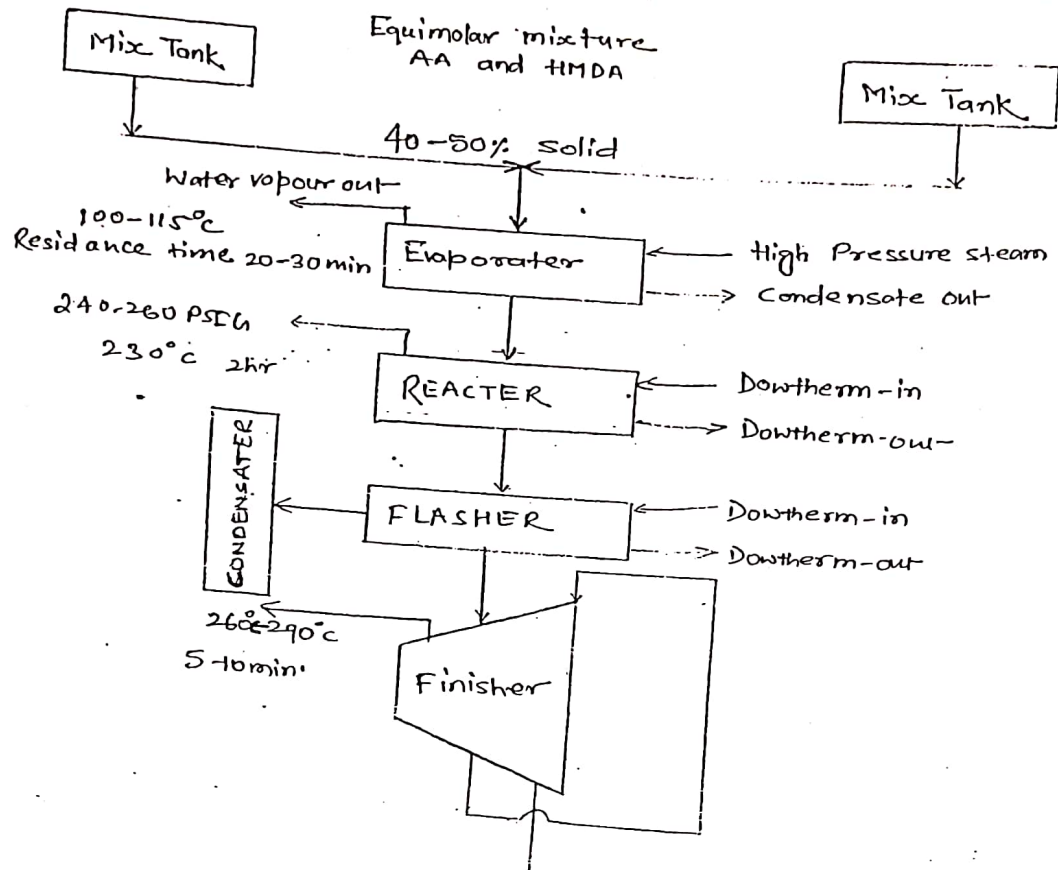


Note:- At  $260^{\circ}\text{C} - 280^{\circ}\text{C}$  the water gets flash evaporated. Pressure builds up. Reduction in pressure favours ~~for~~ forward reaction. At this stage only 90% reaction gets completed above 90% is difficult. In order to facilitate the reaction further the pressure is reduced reduced and water has to be removed and reaction goes upto 99%.

### Continuous Polymerisation Process :-

Continuous polymerisation methods are now available. Most continuous units are chemically engineered versions of the standard multicycle batch technology with separate vessels for different stages.

# Flow sheet of continuous polymerisation plant for Nylon-66



## Comparative merits and demerits of N6 and N66 Production

Sr. No.	PARAMETER	N6	N66
1.	No. of monomer required	one	Two
2.	Availability in India	Available	should be imported.
3.	Adjustive stoichiometric ratio	Not required	<del>not</del> required
4.	Catalyst	Not (H <sub>2</sub> O) required	Not required
5.	Pressure maintenance	Not important	important
6.	Mechanism	Many steps.	simple (two steps)
7.	Completing conversion (%)	90%	> 99%
8.	Post operations	Many	less
9.	Intermediate formation	not required	Required
10.	Purity	Less Pure	Pure
11.	Properties	Not so good as N66	Comparatively better

3rd  
unit

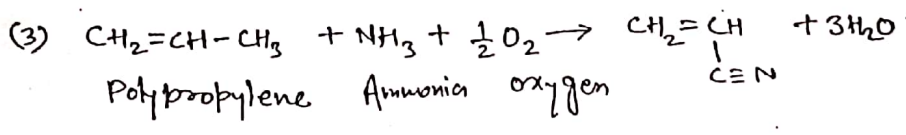
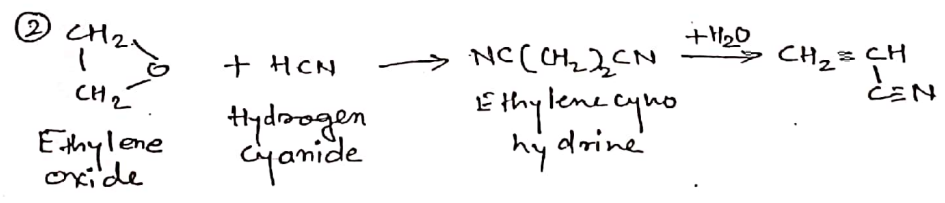
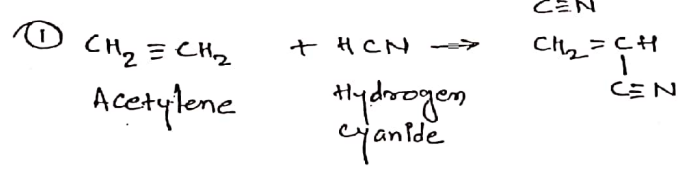
## ACRYLIC FIBRES $(-\text{CH}_2-\underset{\text{C}\equiv\text{N}}{\text{CH}}-)$ (PAN)

Introduction :- Next to polyester and polyamides acrylic fibres occupy the eminent position in the family of manmade fibre. It is justified in the phenomenal growth of acrylics and its popularity through out the world. Acrylic fibres have replaced wool in many applications, particularly in hand knitting and hosiery garments. The majority of yarns are usually bulky yarns which go into the manufacture of pullovers, sweaters, socks etc. Blankets and carpets are other applications where the acrylic fibre competes with wool because of its high elasticity, colour brilliancy, voluminarity, ease of washing, resistance to pilling, good light and color fastness values etc. Because of the above mentioned properties and also due to the ease with which modifications can be made ~~through~~ during synthesis and spinning, finishing, acrylic fibres have experienced a tremendous growth.

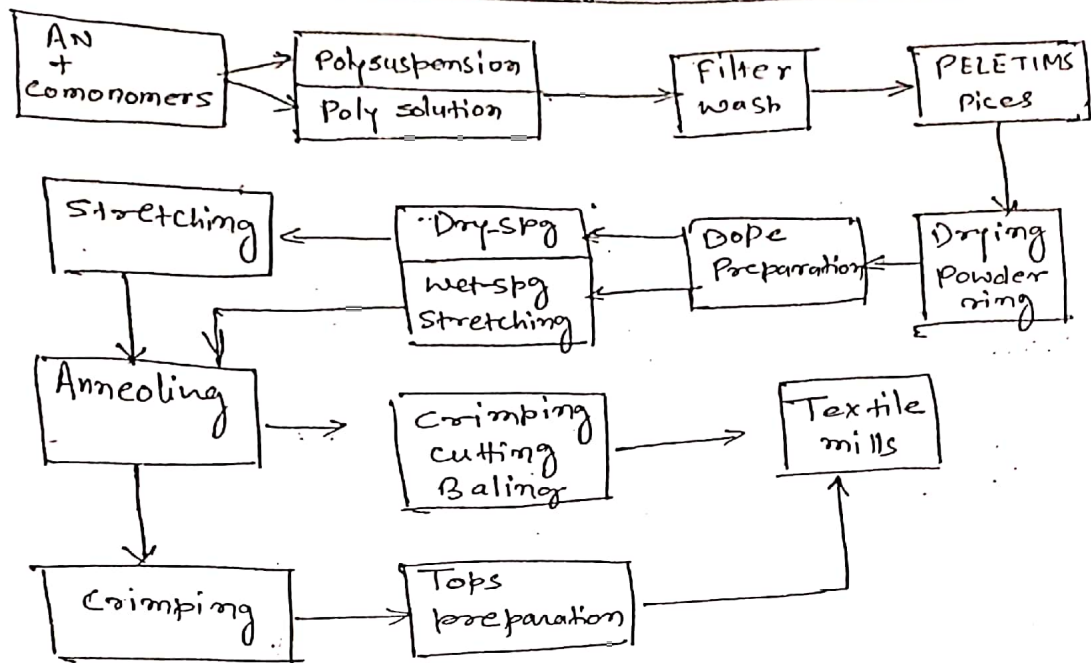
Definition :- The 'acrylic fibre' term refers to a fibre containing at least 85% acrylonitrile (AN) and 15% comonomer while in modacrylics the % of AN must be < 85% but greater than 65%.

### Manufacturing of Raw Material

Acrylonitrile :-  $\text{CH}_2=\underset{\text{C}\equiv\text{N}}{\text{CH}}$



## Flow chart for manufacturing acrylic staple fibre



## Requirement of Comonomer in Acrylic (Poly acrylonitrile) Polymer Production :-

### Problems with homopolymerisation of AN if alone

- (1) Polymerisation is fast. Undergoes thermal degradation during polymerisation liberating lots of heat. Any heat transfer media can not be made useful. So it leads to a degradation product.
- (2) Homo-polymer PAN does not have any dye accepting groups.
- (3) When homopolymer (acrylic) is heated to  $120^{\circ}\text{C}$  it undergoes cyclisation (cyclic compound formation), gives rise to brown to black coloured product which is stable product which is useless as textile fibre and is used as precursor for carbon-fibres.
- (4) Melt spinning (remelt is not possible) is not possible due to above reason.



(5) Homopolymer PAN can not be converted into solution of desired viscosity by dissolving in DMF.

(6) If polymerised in solution or bulk it undergoes autoacceleration. Control of kinetics is difficult. Viscosity suddenly jumps, only 10% conversion takes place and 90% has to be recycled.

So the polymer should be copolymerised which will make it suitable for fibre formation.

Comonomers does following changes :-

- ① Decreases melting point
- ② Increases solubility
- ③ Increases dye affinity
- ④ Increases ease of processing

If comonomer % is increased inherent property of acrylics decreases.

85% AN + 15% Comonomer  $\rightarrow$  Acrylic  
< 85% > 65% AN + < 35% > 15% <sup>comonomer</sup> ~~AN~~  $\rightarrow$  Modacrylic

Plus Points of HOMO PAN

① Even if  $f = 2$  (functionality) the polymer has no MP (high MP, chars without melting), high tensile property.

② On heating heat stability increases

③ Good flame resistance

④ Good oil resistance

Modacrylic :- 60% PAN + 40%  $\approx$  Vinyl chloride

Dynel.

① Self extinguishing

② Chemically resistant

③ Fire resistant.

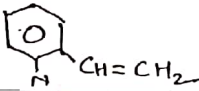
④ Not in Demand

⑤ When it catches fire it produces ~~less~~ poisonous  $Cl_2$  gas.

⑥ Allergy to skin.

Comonomers can be more than two.

### Comonomers Used

Type	Chemical formula	Purpose
(I) NEUTRAL		
① Methyl acrylate (MA)	$CH_2=CH-CO-OCH_3$	1) Increase the solubility
② Methyl methacrylate (MMA)	$CH_2=C(CH_3)-CO-O-CH_3$	2) Open the structure
③ Vinyl acetate	$CH_2=CH-O-OC-CH_3$	3) Increases dyeability
(II) Ionic		
① Sodium methyl Sulphonate (SMS)	$CH_2-\overset{CH_3}{\underset{ }{CH}}-CH_2-SO_3Na$	1) Provides sublimation dye site
② S-allyl-S	$CH_2=CH-CH_2-SO_3Na$	2) Improves differential water sensitivity in bicomponent fibres.
③ S-styrene-S	$CH_2=CH-C_6H_5-SO_3Na$	
④ Itaconic acid	$CH_2=C(\overset{COOH}{ })-CH_2-COOH$	
⑤ 2-Vinyl Pyridine		
(III) Halogen Containing		
① Vinyl Bromide	$CH_2=CH-Br$	1) Imparts flame retardance
② Vinyl chloride	$CH_2=CH-Cl$	2) Mainly used for modacrylics
③ Vinylidene chloride	$CH_2=C(\underset{Cl}{ })-Cl$	

Note: - Vinyl Bromide (VB) - high cost, low strength of the product.  
 Vinylidene chloride (VDC) = has two Cl atoms and got outstanding flame retardance property.

## Some Manufacturing Parameter

(18)

AN = 85%

VA or MA = 10%

Ionic = 5%

M<sub>n</sub> = 40,000 - 60,000

M<sub>w</sub> = 80,000 - 1,40,000

MWD = 1.5 - 3 → Spinnable

### ① Dyeability depends on :-

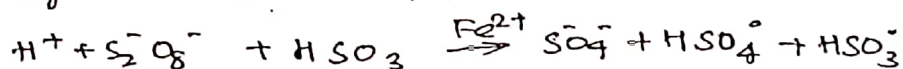
- ① MWD, if MWD is high dye uptake is more and vice-versa.
- ② No. of sulphonate and sulphite fragments in structure
- ③ If M<sub>n</sub> ↑ dye site decreases.
- ④ Low mol. wt. increases dye sites.
- ⑤ Ionic comonomers act as additional dye sites.

### Initiators :-

- ① Free radical type (BPO, AIBN)
  - ① low efficiency.
  - ② slow decomposition
  - ③ suitable for semi and batch process
- ② Redox Initiators :-
  - ① Fast reaction
  - ② High efficiency
  - ③ Reaction can be controlled
  - ④ Low temperature requirement
  - ⑤ Any polymerisation method can be used

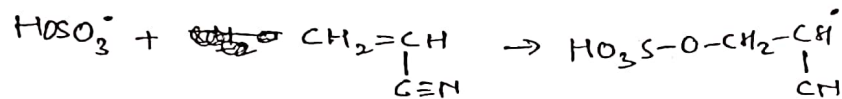
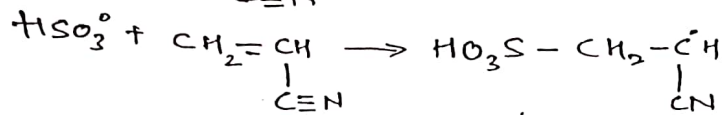
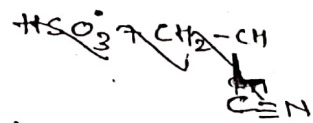
### Mechanism of Polymerisation using Redox initiators

Eg - K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, FeSO<sub>4</sub>, NaHSO<sub>3</sub>

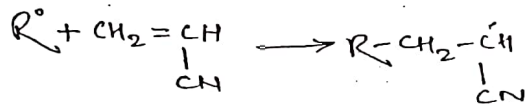


Two radical (bisulphite, bisulfate) are generated.

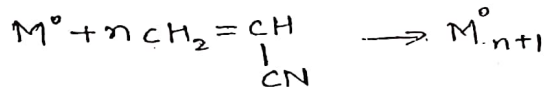
## INITIATION



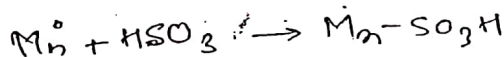
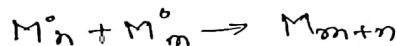
in General,



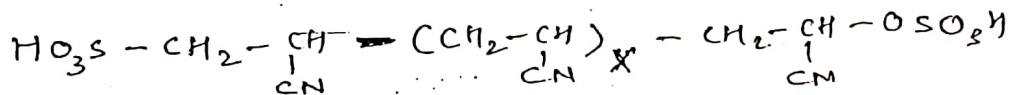
Propagation :-



Termination



Under ideal condition of polymerisation and in absence of chain transfer or disproportionation po chain possess two end groups.



These redox initiators for FR polymerisation serve as the prime functional groups for PAN fibres. Incorporation of acidic end groups (sulfonase and sulfase) in to the polymer chain will help in dyeability of fibres.

## Polymerisation :-

### 1) Bulk Polymerisation

- ① Monomer + Initiator. (M+I)
- ② Difficult to Control
- ③ Bad colour
- ④ Not used in industry

### ② Emulsion Polymerisation

- ① M+I+H<sub>2</sub>O+Emulsifier
- ② Cheap (process)
- ③ impure
- ④ Can not be used for fibre industry.

### ③ Solution Polymerisation

- ① M+I+solvents (DMF)
- ② Costly
- ③ Limitations in mol. wt. (chain transfer)
- ④ Solution can be directly used for spg.
- ⑤ Best when co-ordination catalyst are used.

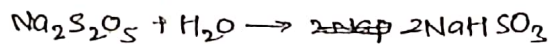
### ④ Suspension Polymerisation

- ① M+I+S+H<sub>2</sub>O (S → suspending agent)
- ② Fast (also can be controlled)
- ③ Cheap (process)
- ④ High molecular wt.
- ⑤ Granular Product can be directly used for dope preparation.
- ⑥ No agglomeration.

## Redox initiator

Most common redox system consists of

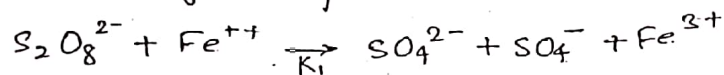
- ① Potassium persulfate ( $K_2S_2O_8$ ) (cheap and easily available)
- ② Sodium bisulfite ( $NaHSO_3$ ) (cheaper) Solid does not



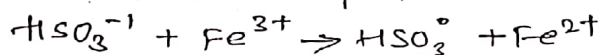
and  $Fe^{++}$  or  $Fe^{+++}$  as catalyst. This system gives added benefit of supplying dyestuffs for fibers.  $pH \rightarrow 2-4$ .

### Reactions

① Oxidation of  $Fe^{++}$  by persulphate<sup>-</sup>



② Reduction of  $Fe^{3+}$  by  $SO_2$  in bisulfite form



Two types of free radicals are produced. Both of them can initiate polymerisation and polymer chain will have bisulfite or persulphate end group. (Further details are explained in previous 2 pages) Theoretically Bisulfite Bisulphite<sup>-</sup> Persulfate of 3/1 to 1/3 is used to have good dye affinity. Due to some problems, in industry ratio of 8/1 to 5/1 is used.

Side reactions :- ① PAN gives pendent  $C \equiv N$  groups giving rise to branching and cross orientation.

② When heated it forms yellow or brown colour.

③ In basic solution it develops colour.

Solving :- Use high monomer concentration, low conversion, faster kinetics.

Limitations - ① If monomer concentration is increased heat transfer is difficult, recycling of converted monomer is difficult. Using full capacity of reactor is difficult.

② Use special redox system such as sodium nitrite/sulphite + Hydrozine salt

Among comonomers methyl acrylate is best. since it gives azeotropic composition. But in India vinyl acetate is used because it is cheap.

MF1.

Polymerisation and spg condition for AN/VA system

① water monomer ratio :- 1.75 - 4.0

② PH = 3.0

③ Bisulphite/persulphate ratio = 4 - 10

④ Reactor Capacity 8.3 litre continuous

⑤  $[\eta]$  DMF at 25°C 1.4 - 1.7

⑥ concentration of Polymer [Wet spg 20-28%  
Dry spg - 25-32%]

additives  $TiO_2$ , Carbon black, metal salts.

⑦ No. of holes in spinnerete = 10,000 - 60,000 - 1,30,000

⑧ size of hole - 0.05 - 0.38 mm

⑨ speed of wet-spg - 20 mts/min

Wet spg.

